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## Using a sulfur-bearing silane to improve rubber formulations for potential use in industrial rubber articles

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The availability of the coupling agent bis (3-triethoxysilylpropyl)-tetrasulfide (TESPT) has provided an opportunity for enhancing the reinforcing capabilities of precipitated amorphous white silica in rubber. Styrene-butadiene rubber, synthetic polyisoprene rubber (IR), acrylonitrile-butadiene rubber, and natural rubber (NR) containing the same loading of a precipitated silica filler were prepared. The silica surface was pretreated with TESPT, which is a sulfur-bearing bifunctional organosilane to chemically bond silica to the rubber. The rubber compounds were subsequently cured by reacting the tetrasulfane groups of TESPT with double bonds in the rubber chains and the cure was optimized by adding sulfenamide accelerator and zinc oxide. The IR and NR needed more accelerators for curing. Surprisingly, there was no obvious correlation between the internal double bond content and the accelerator requirement for the optimum cure of the rubbers. Using the TESPT pretreated silanized silica was a very efficient method for cross-linking and reinforcing the rubbers. It reduced the use of the chemical curatives significantly while maintaining excellent mechanical properties of the cured rubbers. Moreover, it improved health and safety at work-place, reduced cost, and minimized damage to the environment because less chemical curatives were used. Therefore, TESPT was classified as “green silane” for use in rubber formulations.

**Keywords:** sulfur-bearing silane; silica; rubbers; chemical curatives; chemical bonding; reinforcement; green compounds; environment

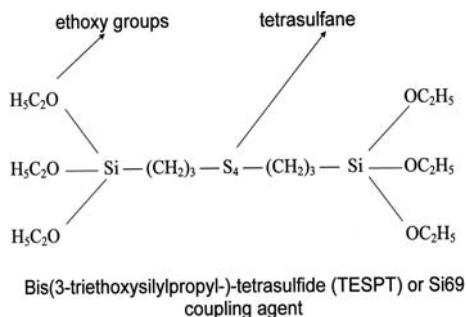
### 1. Introduction

Reinforcing fillers and chemical curatives perform two important functions in rubbers. Reinforcing fillers enhance the processing and mechanical properties of rubber compounds, for example, viscosity, hardness, tensile and fracture properties, abrasion resistance, and modulus. This makes rubber compounds suitable for use in tires, hoses, and conveyor belts [1,2]. Chemical curatives such as sulfur, accelerators, and activators react together at elevated temperatures to produce cross-links between rubber chains [3,4]. Among the reinforcing fillers, short fibers, colloidal carbon blacks, clay, and synthetic silicas are the most widely used in rubber reinforcement. Carbon black (CB) and silica particles have surface areas ranging from 6 to 250 m<sup>2</sup>/g and 125 to 200 m<sup>2</sup>/g, respectively [5–8].

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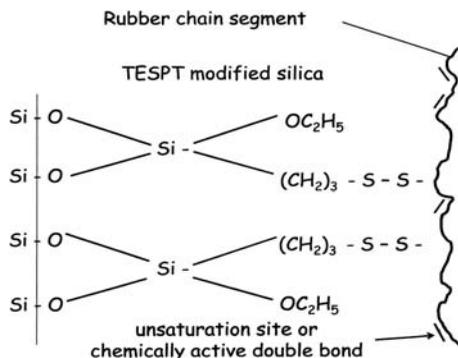
This article was originally published with errors. This version has been corrected. Please see Corrigendum (<http://dx.doi.org/10.1080/01694243.2013.766446>).



Scheme 1. Chemical structure of bis (3-triethoxysilylpropyl)-tetrasulfide (TESPT).

Colloidal carbon blacks have been used extensively to reinforce mechanical properties of rubbers and are being replaced by synthetic silicas. Synthetic silicas are acidic [9] and moisture adsorbing [10] because they have silanol or hydroxyl groups on their surfaces, which are both detrimental to the cure of rubber compounds and can also cause loss of cross-link density in sulfur-cured rubbers [11]. For these reasons, use of silica in rubber products was hampered until bifunctional organosilanes were available. Bifunctional organosilanes are used as primers for treating silica surfaces to make the filler more suitable for use in rubber [12]. The silanization reaction of silica takes place in two different ways. Firstly, silica and silane are mixed together in the required ratio and homogenized in an additional, preliminary mixing stage. The modification is carried out at the optimum temperature and reaction time. Or, silanization is carried out *in situ*. This is usually done in an internal mixer in the first stage of mixing, where the liquid silane is added together with, or after the addition and dispersion of the silica. This process is carried out within the specified limits of temperature increases in the mixer and strict mixing times [13,14].

Bifunctional organosilanes, such as bis(3-triethoxysilylpropyl)-tetrasulfide (TESPT), known also as Si69 coupling agent, have been used extensively with silica in rubber compounds. TESPT has a fast cure kinetics and ability to form disulfidic rubber-to-filler bonds [12,15]. This silane possesses tetrasulfane and ethoxy groups (Scheme 1). The tetrasulfane groups react with the rubber in the presence of accelerators at elevated temperatures, i.e. 140–240 °C, with or without elemental sulfur being present, to form cross-links in unsaturated rubbers such as natural rubber. The ethoxy groups react with the silanol groups on the surface



Scheme 2. Silanized silica nanofiller pretreated with TESPT. Tetrasulfane groups react with rubber chains to form stable covalent sulfur bonds.

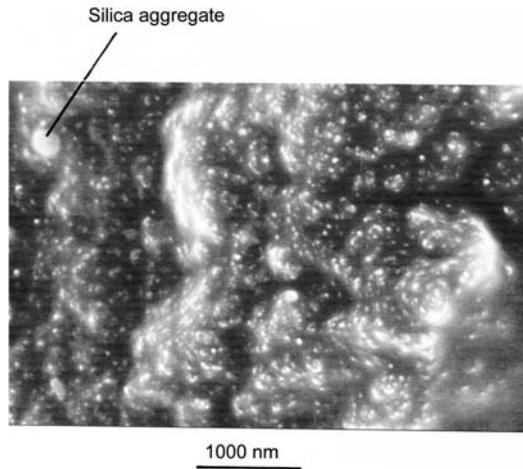


Figure 1a. SEM micrograph showing poor dispersion of silica particles in the rubber. Note the large silica aggregates in the rubber. Data for the SBR. Mixing time = 4 min.

of this filler during compounding to form stable filler/TESPT bonds (Scheme 2). The TESPT reaction with silanol groups reduces their numbers, and the remaining groups become less accessible to the rubber because of steric hindrance. These changes reduce the viscosity of rubber compounds and improve their cure properties [12,16]. Moreover, this combines filler and sulfur into a single product known as “cross-linking filler”. One such filler is precipitated amorphous white silica the surface of which is pretreated with TESPT to chemically bond silica to rubber. This also forms an integral part of curing systems to improve the cross-linking network properties [17].

Koenig and Parker [18] measured effects of pretreated silanized silica, and silica and liquid silane mixture on the vulcanization of a sulfur-cured polyisoprene. In the latter case, the silanization was carried out *in situ*. They concluded that the rubber mixed with the pre-

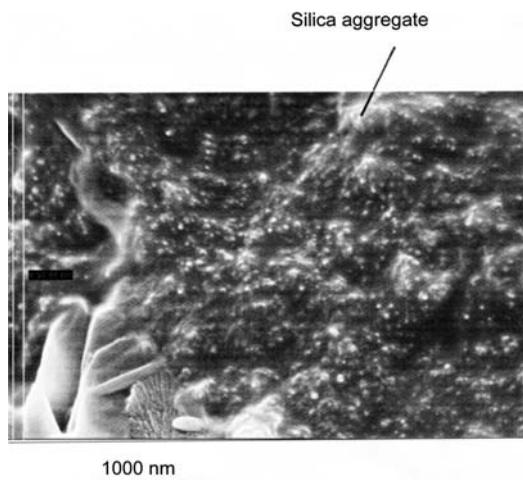


Figure 1b. SEM micrograph showing improved dispersion of silica particles in the rubber. Note small silica aggregates in the rubber. Data for the SBR. Mixing time = 7 min.

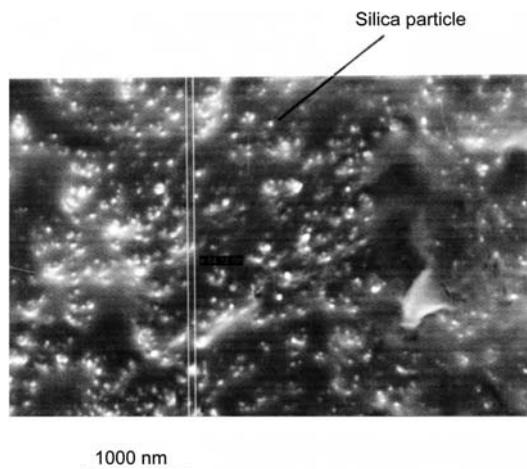


Figure 1c. SEM micrograph showing good dispersion of silica particles in the rubber. Data for the SBR. Mixing time = 10 min.

treated silanized silica had a higher cross-link density and increased filler–rubber interaction both of which were beneficial to the mechanical properties of the cured rubber.

The aim of this study was to use a high loading of precipitated silica pretreated with TESPT to cross-link and reinforce the mechanical properties of styrene-butadiene rubber (SBR), synthetic polyisoprene rubber (IR), acrylonitrile-butadiene rubber (NBR), and natural rubber (NR). A sulfenamide accelerator and two activators were added to optimize the chemical bonding between the silica and rubbers via the tetrasulfane groups of TESPT, and the mechanical properties of the cured rubbers were measured to assess effect of the filler on the rubber properties.

## 2. Experimental

### 2.1. Materials

The raw rubbers used were standard Malaysian natural rubber (NR) grade L (98 wt.% cis-1–4 content), styrene-butadiene rubber (SBR) (23.5 wt.% styrene; Intol 1712, Polimeri Europa UK Ltd, Hythe, UK), synthetic polyisoprene rubber (minimum 96 wt.% cis- 1–4 content; Kraton IR- 307, Kraton Polymers UK Ltd, UK), and nonstaining cold polymerized acrylonitrile-butadiene rubber (NBR) (26% by weight acrylonitrile; Krynac 2645F; LANXESS Europe GmbH, Germany). SBR 1712 is a cold emulsion copolymer, polymerized using a mixture of fatty acid and rosin acid soaps as emulsifiers. It is extended with 37.5 phr of highly aromatic oil and contains a styrenated phenol as a nonstaining antioxidant. It has approximately 4.8% by weight organic acid. Viscosities of the raw rubbers were: SBR, 54 MU; IR, 69 MU; NBR, 45 MU; and NR, 97 MU, where MU stands for Mooney Units. This information was provided by the suppliers.

The reinforcing filler was Coupsil 8113 (Evonik Industries AG, Germany). Coupsil 8113 is precipitated amorphous white silica-type Ultrasil VN3 surface of which had been pretreated with TESPT. It has 11.3% by weight TESPT, 2.5% by weight sulfur (included in TESPT), 175 m<sup>2</sup>/g surface area (measured by N<sub>2</sub> adsorption), and a 20–54 nm particle size.

In addition to the raw rubbers and filler, the other ingredients were *N*-tert-butyl-2-benzothiazole sulfenamide (a safe-processing delayed action nonsulfur donor accelerator with a melting point of 109 °C) (Santocure TBBS, Flexsys, Dallas, TX), zinc oxide (ZnO; an activator, Harcros Durham Chemicals, Durham, UK), stearic acid (an activator, Anchor Chemicals, Manchester, UK), *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine (6PPD, an antidegradant, Santoflex 13, Monsanto, Brussels, Belgium), and heavy paraffinic distillate solvent extract containing aromatic oils (a processing oil, Enerflex 74, BP Lubricants & Special Products Limited, Milton Keynes, UK). The oil was added to reduce the rubber viscosity, and the antidegradant to protect the rubbers against environmental ageing. The cure system consisted of TBBS, ZnO, and stearic acid, which were added to fully cross-link the rubbers.

### **2.2. Determination of the internal double bonds in the raw SBR, NBR, IR, and NR rubbers using nuclear magnetic resonance spectroscopy**

The overall level of internal double bonds in the raw rubbers was determined by liquid state nuclear magnetic resonance (NMR) spectroscopy (Bruker Advance II, 300 MHz, Bruker, UK). About 10 mg of each raw rubber was dissolved in a suitable deuterated solvent (chloroform- $d_1$  for the IR, NBR, and NR, and tetrachloroethane- $d_2$  for the SBR). Hydrogen NMR spectra were obtained with 30 degree pulse, 6 s delay between pulses and 256 scans. The butadiene in the NBR and SBR showed two sets of signals for the  $-\text{CH}=\text{CH}-$  and  $\text{CH}=\text{CH}_2$ . The IR showed two sets of signals for the isoprene 1,4 cis  $\text{CH}=\text{}$  and low level of vinyl groups. In each case, the peak area integrals were corrected for the relative number of hydrogen atoms in each group and expressed as mole% fraction double bond in relation to all chemical groups in the rubber.

### **2.3. Mixing**

The rubber compounds were mixed in a Haake Rheocord 90 (Berlin, Germany), a small size laboratory mixer with counter-rotating rotors. The Banbury rotors and the mixing chamber were set initially at 23 °C for mixing the SBR, IR, and NBR compounds, and at 48 °C for mixing the NR compound. The raw NR was hard because it had a high viscosity and for this reason, the NR compound was mixed at a higher initial temperature. The rotor speed was set at 45 rpm. The volume of the mixing chamber was 78 cm<sup>3</sup>, and it was 57% full during mixing. Polylab Monitor 4.17 software was used for controlling the mixing condition and storing data.

### **2.4. Assessment of the silica dispersion in the rubber by scanning electron microscope**

To select a suitable mixing time for incorporating silica in the rubbers, the rubbers were mixed with 60 phr TESPT pretreated silanized silica. The filler was introduced first into the mixer and then the raw rubber was added to prevent the silica powder from escaping the small chamber of the mixing machine as the ram was lowered. The filler and raw rubbers were mixed together when the viscosity of the rubbers was still relatively high, which led to an improved dispersion [19]. The mixing time was increased to 22 min to measure the time needed to disperse the silica particles well in the rubbers. Twenty-four hours after mixing ended, the rubbers were examined in a scanning electron microscope (SEM) to assess the filler dispersion.

Dispersion of the silica particles in the rubber was assessed by a Cambridge Instruments Stereoscan 360 Tungsten Filament SEM. Small pieces of the uncured rubbers were placed in liquid nitrogen for 3 min. They were recovered and fractured into two pieces to create fresh surfaces. The samples, 58 mm<sup>2</sup> in area and 6 mm thick, were coated with gold, and then examined in the SEM. The degree of dispersion of the silica particles in the rubber was subsequently studied from the SEM micrographs. After the SEM micrographs were examined, suitable mixing times were used for adding the filler to the rubbers. For example, Figures 1a–1c show dispersion of the silica particles in the SBR improving with time. Evidently, after 10 min mixing, the silica particles dispersed well in the rubber matrix.

### 2.5. Addition of TBBS to the silica-filled rubbers

Accelerators are ingredients used to control the onset and rate of cure and the cross-link density in rubber. To activate the rubber reactive tetrasulfane groups of TESPT (Scheme 2), TBBS was added. The loading of TBBS in the silica-filled rubbers was increased progressively to 9 phr to measure the amount needed to optimize the chemical bonding between the rubber and TESPT and to increase the cross-link density in the rubber. The formation of cross-links strengthened the rubber/filler interaction [12]. In total, 39 rubber compounds were made.

### 2.6. Addition of ZnO to the silica-filled rubbers with TBBS

Zinc oxide enhances the action of organic accelerators in rubber during curing and is regarded as an activator. The loading of ZnO in the silica-filled rubbers with TBBS was raised to 2 phr to determine the amount needed to maximize the efficiency of TBBS and to optimize the chemical bonding between the filler and rubber. In total, 29 rubber compounds were mixed.

Table 1. Mixing conditions for the rubber compounds.

Compound	Mixing cycle
1	SBR was mixed with processing oil for 2 min and then silica was added and mixed for another 2 min. Finally, the chemical curatives and antidegradant were added and mixed for another 6 min. The compound temperature reached 63 °C during mixing.
2	IR was mixed with silica for 17 min and then the chemical curatives and antidegradant were added and mixed for another 3 min. The compound temperature reached 56 °C during mixing.
3	NBR was mixed with silica for 17 min and then the chemical curatives and antidegradant were added and mixed for another 3 min. The compound temperature reached 80 °C during mixing.
4	NR was mixed with silica for 13 min and then the chemical curatives and antidegradant were added and mixed for another 3 min. The compound temperature reached 85 °C during mixing.

Chemical curatives: *N*-tert-butyl-2-benzothiazole sulfenamide (TBBS), zinc oxide (ZnO), and stearic acid. Antidegradant: *N*-(1,3-dimethylbutyl)-*N'*-phenyl-*p*-phenylenediamine. Note that the silica surface was pretreated with TESPT before it was mixed with the rubbers.

### 2.7. Addition of stearic acid to the silica-filled rubbers with TBBS and ZnO

Stearic acid is a fatty acid that is added as a coactivator with ZnO in sulfur vulcanization. It is assumed that stearic acid reacts with ZnO to form zinc stearate, which is an essential cure activator. Stearic acid also acts as a plasticizer and internal lubricant between polymer chains, and aids dispersion of carbon black and other fillers in the rubber. It is used as release agent and lubricant for rubber compounds. The loading of stearic acid in the silica-filled rubbers with TBBS and ZnO was increased to 2 phr to measure the amount needed to increase the dispersion and solubility of ZnO and enhance the efficiency of the curing reaction in the rubbers. In total, 20 rubber compounds were prepared.

After these measurements were completed, four rubber compounds were prepared for further tests. Full details of the mixing conditions are summarized in Table 1. These compounds were chosen because they had the optimum loadings of TBBS and ZnO in them (Table 2). To mix the IR, NBR, and NR compounds, the filler was placed in the mixing chamber, and then the raw rubbers were added. As mentioned earlier, this prevented the silica powder from escaping the mixing chamber when the ram was lowered. The chemical curatives and antidegradant were added subsequently. Note that the mixing route for the SBR compound differed from the other compounds. Processing oil was mixed with the raw rubber first and then silica was added. This was a more convenient way of adding oil to the rubber in such a small mixer. Finally, when mixing ended, the rubbers were removed from the mixer and milled to a

Table 2. Recipe for the rubber compounds, Mooney viscosity at 100°C and cure properties at 140 °C.

Formulation (phr)	Compound			
	1	2	3	4
SBR Intol 1712	100	–	–	–
IR 307	–	100	–	–
NBR	–	–	100	–
SMRL (NR)	–	–	–	100
Silica + TESPT	58.5	58.5	58.5	58.5
Sulfur (in TESPT)	1.5	1.5	1.5	1.5
TBBS	3	7	4	6
ZnO	0.5	1	0.3	0.3
6PPD	1	1	1	1
Processing oil	5	–	–	–
<i>Cure system</i>				
S(phr)/TBBS(phr)/ZnO(phr)	1.5/3/0.5	1.5/7/1	1.5/4/0.3	1.5/6/0.3
Double bond content (mole%)	19.1	21.0	27.0	25.0
<i>Mooney viscosity (MU)</i>				
	71	105	107	106
<i>ODR results</i>				
Minimum torque (dN m)	18	26	26	26
Maximum torque (dN m)	56	137	101	107
Δtorque (dN m)	38	111	75	81
Scorch time, $t_{s2}$ (min)	16	8	23	9
Optimum cure time, $t_{95}$ (min)	80	34	80	27
Cure rate index ( $\text{min}^{-1}$ )	1.6	3.9	1.7	5.6

<sup>a</sup>Sulfur is included in TESPT. Silanized silica composition: silica, 53.22 phr; TESPT, 6.78 phr; sulfur 1.5 phr (in TESPT).

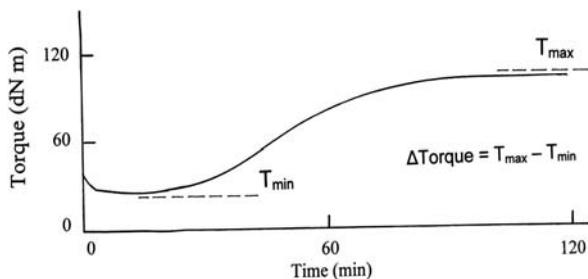


Figure 2. A typical torque vs. time cure trace for the NBR produced at 140 °C in the ODR.

thickness of about 6–8 mm. The compounds were next stored at  $21 \pm 2$  °C for at least 24 h before their viscosity and cure properties were measured.

### 2.8. Viscosity and cure properties of the rubber compounds

The viscosity of the rubber compounds was measured according to British Standard 1673: Part 3; London, UK (1969), and the results were expressed in Mooney Units (MU). The scorch time, which is the time for the onset of cure, and the optimum cure time, which is the time for the completion of cure, were determined from the cure traces generated at  $140 \pm 2$  °C by an oscillating disk rheometer (ODR) curemeter. This test was carried out according to British Standard 1673: Part 10; London, UK (1977). The cure rate index, which is a measure of the rate of cure in the rubber, was calculated using the method described in British Standard 903: Part A60: Section 60.1; London, UK (1996). Figure 2 shows a typical cure trace produced at 140 °C for the NBR (compound 3; Table 2).  $\Delta$ torque, which is the difference between the maximum and minimum torque values on the cure traces of the rubbers and is an indication of cross-link density changes in the rubber, was subsequently plotted against the loading of TBBS, ZnO, and stearic acid for the four rubbers.

### 2.9. Test pieces and test procedure

After the viscosity and cure properties were measured (Table 2), the rubber compounds were cured in a compression mold at 140 °C with a pressure of 11 MPa. Pieces of rubber, each ~140 g in weight, were cut from the milled sheets. Each piece was placed in the center of

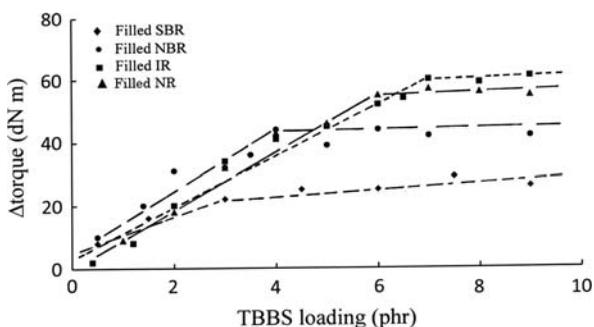


Figure 3.  $\Delta$ torque vs. TBBS loading for the SBR, IR, NBR, and NR rubber compounds. Each point on the figure corresponds to one compound.

the mold to enable it to flow in all the directions when pressure was applied. This prevented anisotropy from forming in the cured rubber. For determining the mechanical properties of the rubbers, sheets of rubber 23 cm  $\times$  23 cm and approximately 2.5 mm thick were used from which various samples for further tests were cut.

### 2.10. Measurement of the mechanical properties of the cured rubbers

To measure the mechanical properties of the cured rubbers, the following British Standards were used:

- Hardness: British Standard 903: Part A26, London, UK (1995).
- Tensile properties and tensile modulus at different strain amplitudes: British Standard 903: Part A2, London, UK (1995).
- Tear energy: British Standard 903: Part A3, London, UK (1995).

## 3. Results and discussion

### 3.1. Comparing effects of TBBS, ZnO, and stearic acid on the $\Delta$ torque of the silica-filled SBR, NBR, IR, and NR rubbers

Figure 3 shows  $\Delta$ torque as a function of TBBS loading for the SBR, IR, NBR, and NR rubbers. For the SBR,  $\Delta$ torque was increased from 8 to 22 dN m when the loading of TBBS reached 3 phr. Thereafter,  $\Delta$ torque was increased at a much slower rate to 26 dN m as the loading of TBBS was raised to 9 phr. Evidently, 3 phr TBBS was sufficient to start and optimize the reaction between the tetrasulfane groups of TESPT and the rubber. Similarly, for the IR, NBR, and NR, 7 phr, 4 phr, and 6 phr TBBS, respectively were needed to maximize chemical bonding between the silica and rubber chains.

For the SBR with 3 phr TBBS, the addition of ZnO improved the efficiency of TBBS, and  $\Delta$ torque was increased sharply from 22 to 57 dN m as the loading of ZnO was raised to 0.5 phr. However, the rate of increase of  $\Delta$ torque slowed down considerably with  $\Delta$ torque rising from 57 to 62 dN m as the amount of ZnO reached 2 phr (Figure 4). It was concluded that 0.5 phr ZnO was sufficient to optimize the efficiency of TBBS and increases the chemical bonding between the silica and rubber chains. Likewise, for the IR with 7 phr TBBS and NBR with 4 phr TBBS, 1 phr ZnO and 0.3 phr ZnO, respectively enhanced the efficiency of

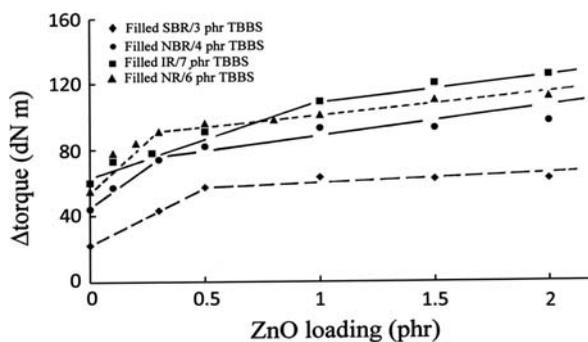


Figure 4.  $\Delta$ torque vs. zinc oxide loading for the SBR, IR, NBR, and NR rubber compounds with TBBS.

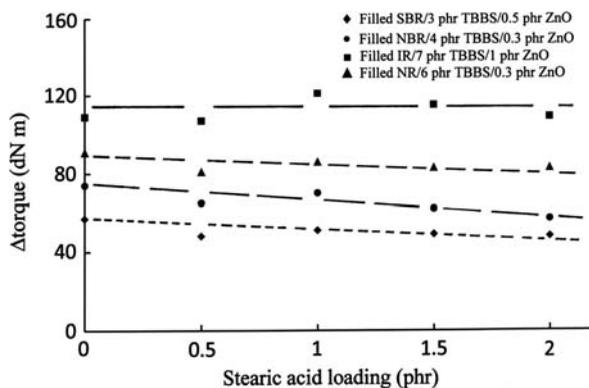


Figure 5.  $\Delta$ torque vs. stearic acid loading for the SBR, IR, NBR, and NR rubber compounds with TBBS and ZnO.

cure and formation of the covalent sulfur bonds between the silica and rubber. The NR with 6 phr TBBS required 0.3 phr ZnO to achieve a similar effect.

The addition of stearic acid to the SBR, IR, NBR, and NR rubbers with TBBS and ZnO had no benefit for the  $\Delta$ torque at all (Figure 5). The decrease in  $\Delta$ torque as a function of the loading of stearic acid could be due to the plasticization effect of the stearic acid. For the SBR with 3 phr TBBS and 0.5 phr ZnO,  $\Delta$ torque decreased from 57 to 46 dN m as the loading of stearic acid reached 2 phr. A similar trend was also seen for the NBR with 4 phr TBBS and 0.3 phr ZnO, and NR with 6 phr TBBS and 0.3 phr ZnO. Though, for the IR with 7 phr TBBS and 1 phr ZnO,  $\Delta$ torque did not appear to change and remained at about 110 dN m when up to 2 phr stearic acid was added. Since stearic acid did not increase the  $\Delta$ torque or cross-link density of the rubbers, it can be removed from the formulation.

Synthetic polyisoprene rubber (IR) is the synthetic analog of NR and is chemically and structurally similar to it. IR has been used in the same applications as NR such as in blends with styrene-butadiene rubber and polybutadiene rubber to improve their processibility, and also mineral filled IR is used in footwear, sponge, and sporting goods [20]. It was interesting to note that the NR required 1 phr less TBBS and 0.7 phr less ZnO than the IR to react the rubber reactive tetrasulfane groups of TESPT with the rubber chains to form chemical bonding between the two. Evidently, the TBBS and ZnO requirements for curing the NR were lower in spite of the rubber being chemically and structurally similar to its synthetic analog IR and having  $\sim 19\%$  more double bonds (Table 2). This was a useful finding.

As stated earlier, Coupsil 8113 has 2.5 wt% sulfur, which is included in TESPT. This was equivalent to 1.5 phr sulfur in the formulation. This study showed that at a constant loading of sulfur, i.e. 1.5 phr, the amounts of TBBS and ZnO needed to fully cure the rubbers depended on the rubber composition as expected. The S/TBBS/ZnO requirement for the rubbers was: SBR (1.5 phr/3 phr/0.5 phr); IR (1.5 phr/7 phr/1 phr); NBR (1.5 phr/4 phr/0.3 phr); and NR (1.5 phr/6 phr/0.3 phr). This information is vitally important to rubber formulation scientists who use chemical curatives to cross-link rubbers and came to light when TESPT pre-treated silanized precipitated silica was used.

Table 3. Mechanical properties of the cured rubbers shown in Table 2.

Properties	Compound			
	1	2	3	4
Hardness (Shore A)	62	80	70	75
Tensile strength (MPa)	26	17	28	37
Elongation at break (%)	1308	404	973	837
Stored energy density at break ( $\text{mJ/m}^3$ )	140	33	115	137
Tear energy ( $\text{kJ/m}^2$ )	75	17	40	58
Range of values ( $\text{kJ/m}^2$ )	71–89	10–23	37–43	46–95
Modulus at different strain amplitudes (MPa)				
Strain amplitude (%)				
100	0.73	3.0	1.8	2.23
200	0.93	3.7	2.0	3.16
300	1.17	4.3	2.5	4.23

### 3.2. Effect of silanized silica nanofiller on the mechanical properties of the cured SBR, NBR, IR, and NR rubbers

Table 3 shows the mechanical properties of the cured rubbers. The hardness of the cured SBR, IR, NBR, and NR were 62, 80, 70, and 75 Shore A, respectively. The tensile strength and elongation at break were 26, 17, 28, and 37 MPa, and 1308, 404, 973, and 837%, respectively. The properties related to fracture, i.e. stored energy density at break and tear energy were 140, 33, 115, and 137  $\text{mJ/m}^3$ , and 75, 17, 40, and 58  $\text{kJ/m}^2$ , respectively. The tensile modulus of the four rubbers increased as a function of the strain amplitude. For the SBR, the modulus rose from 0.73 to 1.17 MPa, for the IR, from 3.0 to 4.3 MPa, for the NBR, from 1.8 to 2.5 MPa, and for the NR, from 2.23 to 4.23 MPa as the strain amplitude was raised from 100 to 300%. Interestingly, these properties were better than those reported previously for sulfur-cured NR and SBR rubbers reinforced with 60 phr precipitated silica and up to 10 phr liquid TESPT. The cure system in the NR compound consisted of four chemical curatives adding up to 10.1 phr, and in the SBR compound five chemical curatives adding up to 9.1 phr. The silica was reacted with liquid TESPT *in situ*, which generated harmful ethanol during mixing [21–22]. However, this problem was remedied when TESPT pretreated silanized silica was used. It appeared that reducing the excessive amounts of the chemical curatives had no adverse effect on the rubber properties and in fact using the TESPT pretreated silanized silica produced better quality rubber compounds and ethanol free mixing.

The results for the NR and IR rubbers were also interesting. The IR was harder and had a slightly higher modulus at different strain amplitudes but the other properties were inferior (Table 3). Rubber properties, for example, tensile strength, and stored energy density at break increase, reaching a maximum, and then deteriorate substantially as a function of cross-link density [3,4]. The  $\Delta$ torque of the IR was 27% higher than that of the NR, which indicated a higher cross-link density and thus a harder rubber (Table 2). The inferior properties of the IR were due to the excessive cross-links. NR crystallizes much faster than IR although their chemical constitution is similar, which might have also contributed to the superior properties of the NR vulcanizates [23]. The strength of NR and IR depends on their crystallizability during deformation. However, ability to crystallize on stretching will be severely hampered if there are too many cross-links in the rubber [24]. The much larger cross-link density of the IR indicated that the rubber did not benefit from crystallization as much as the NR did. It was also noted that the scorch and optimum cure times of the rubber compounds were too

high for practical uses, e.g. see data for the NBR shown in Figure 2 and Table 2. Though, cure cycles can be made much shorter by increasing temperature.

Sulfur vulcanization can only be applied to rubbers with unsaturation or double bond in the backbone or to rubbers with unsaturated side groups [25]. Various techniques have been applied to measure the internal double bonds in rubbers. For instance, in one study, the internal double bonds of some raw SBR, IR, and NR rubbers were measured by perbenzoic acid addition. The SBR contained 77–78%, IR 88–89%, and NR 94–95% double bonds, respectively [26]. The raw SBR, NBR, IR, and NR rubbers used in this study had 19.1 mol%, 27.0 mol%, 21.0 mol%, and 25 mol% of double bonds, respectively. Surprisingly, there was no obvious correlation between the double bond content and the TBBS requirement for the optimum cure of the rubbers. This was disappointing because correlation between the two could have helped to calculate the actual TBBS requirement for the optimum cure of the rubbers using exclusively the double bond content and avoid the extensive practical procedures described in this study.

Rubber reinforcement is due to filler–rubber interaction [11,27], filler–filler interaction [28], and formation of cross-links in rubber [29,30]. The  $\Delta$ torque values of the SBR, IR, NBR, and NR rubbers were 38–111 dN m (Table 2) and this confirmed contribution from the chemical bonding or cross-links between the rubber and filler to the rubber properties [31]. The silica particles were dispersed well in the rubber matrix (e.g. Figure 1c), and this was beneficial to the mechanical properties of the cured rubber [32]. Since the formation of stable covalent sulfur bonds between silica and rubber produces strong rubber–filler interaction [17], it was essential to optimize the chemical bonding between the two. As the  $\Delta$ torque values in Table 2 indicate, when the tetrasulfane groups of TESPT reacted with the rubber chains and the reaction was maximized by using sufficient amounts of TBBS and ZnO, this optimized the rubber–filler interaction and at the same time, it helped to reduce the excessive use of these harmful chemicals, and eliminated elemental sulfur and stearic acid from the formulation altogether.

### 3.3. Health, safety, and the environmental issues related to rubber compounds

Excessive use of the chemical curatives is harmful to health, safety, and the environment and their use is restricted by the new European chemicals policy, Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) and various legislations for environment and safety. For example, the rubber formulation for emission control hose tube (ECHT) contains NBR, 100 phr; carbon black and silica, 60 phr (50 phr CB and 10 phr silica); chemical curatives, 11.75 phr (two accelerators, 5.5 phr; two activators, 6 phr; elemental sulfur, 0.25 phr); and antidegradants and processing aids, 76.4 phr [33]. The chemical curatives are about 6.25 wt.% in the formulation. Note that there is a low level of polycyclic aromatic hydrocarbons (PAH) within the structure of carbon black. Many of these PAHs are tightly bound into the structure of the CB aggregate and are not free to migrate, but a small amount will be on the surface. PAHs are known to be highly carcinogenic (cause cancer), mutagenic (cause mutation), and teratogenic (cause birth defects) and therefore there is a considerable health risk associated with their use in rubber compounds [34]. If CB and chemical curatives in the ECHT formulation were replaced with silica, and 4.0 phr TBBS and 0.3 phr ZnO, respectively, and the other additives retained, it would reduce the number of the chemical curatives to two. On this basis, the total weight of the curatives in the formulation would be reduced to about 2.29 wt.%, which is a significant decrease. In addition, a large reduction in the use of ZnO, elimination of elemental sulfur and stearic acid that is often used as a coactivator with ZnO, and replacement of carbon black with precipitated silica would ultimately lower cost,

improve health and safety at work-place, and minimize damage to the environment. This will be a major step towards manufacturing green and environmental-friendly ECHTs.

#### 4. Conclusions

From this study, it is concluded that:

- Using the sulfur-bearing TESPT pretreated precipitated silica filler to cross-link and reinforce the SBR, IR, NBR, and NR rubbers reduced the excessive use of TBBS and ZnO, and eliminated elemental sulfur and stearic acid from the formulation altogether. This, in turn, improved health and safety at work-place, reduced cost, and minimized damage to the environment. Therefore, TESPT can be classified as “green silane” for use in rubber formulations.
- The use of the sulfur-bearing TESPT pretreated precipitated silica helped to measure accurately the optimum amounts of TBBS and ZnO needed for fully curing the SBR, IR, NBR, and NR rubbers. Notably, at a constant loading of sulfur (in TESPT), there was no clear correlation between the TBBS requirement to attain optimum cure and the internal double bond content of the rubbers. Though, it must be noted that this may be true only for these dissimilar rubbers.

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